Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) EP 1 245 533 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication: 02.10.2002 Bulletin 2002/40

(51) Int Cl.7: C01B 3/50, F25J 3/02

(21) Application number: 02076094.8

(22) Date of filing: 20.03.2002

(84) Designated Contracting States:

AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU

MC NL PT SE TR

Designated Extension States:

AL LT LV MK RO SI

(30) Priority: 21.03.2001 US 277596 P 09.04.2001 US 282627 P

26.12.2001 US 35709

(71) Applicant: L'air Llquide, S.A. à Directoire et Conseil de Surveillance pour l'Etude et l'Exploitation des Procédés Georges Claude 75321 Paris Cedex 07 (FR) (72) Inventor: Granier, Francois Houston, Texas 77042 (US)

(74) Representative: Mercey, Fiona Susan et al L'Air Liquide SA, Direction de la Propriété Intellectuelle, 75, Quai d'Orsay 75321 Paris Cedex 07 (FR)

(54) Methods and apparatus for treatment of synthesis gas and related gases

(57) An improved methane wash process is disclosed wherein a reduced amount of methane wash is required, thereby allowing for savings in energy costs in operation of the cycle and capital costs in constructing the cycle by removing an intermediate gaseous stream

from the methane wash column (2, 62). Further embodiments allow for an energy recovery and an enhanced recovery of a carbon monoxide and/or hydrogen product.

EP 1 245 533 A1

[0001] The present invention relates to methods and apparatus for treating synthesis gas;

[0002] For purposes of this patent, the following terms are defined. As used herein, the term "air separating unit" or "air separation unit" means and refers to a facility, plant, location or process for separating the components of a feed gas and may include both cryogenic and non-cryogenic facilities. The term "contaminant" means and refers to components of a gas that are undesired in the final product.

[0003] The term "feed gas" means and refers to a gas fed to a process or distillation apparatus. The term "cold box process" means and refers to processes to purify carbon monoxide ("CO") and/or hydrogen ("H₂"). The term "methane wash" means and refers to a type of cold box process. The term "syngas" means and refers to synthetic and/or synthesis gas containing at least H₂ and CO. Syngas is commonly produced by catalytic conversion or partial oxidation of a hydrocarbon.

[0004] Generally, cold box efficiencies are measured by several factors. In a classical cold box utilizing a methane wash, the performance of a methane wash cold box is most often measured by, but not limited to:

- CO recovery (this parameter has a direct impact on the quantity of feedstock required to generate the syngas)
- Power consumption required to produce refrigeration and separation/purification of the products usually through a CO (or N₂) refrigeration cycle including a compressor and a cryogenic expander.

[0005] Often, a desired end product H_2/CO ratio does not match the H_2/CO ratio of the syngas feed gas. Quite commonly, an excess of H_2 is produced. This excess H_2 is then required to be disposed of through burning, for example as a fuel in a reformer and/or the like or disposed of elsewhere. The prior art has arrived at various solutions to this problem.

[0006] Commonly, membrane-based permeation units are installed upstream of the cold box in a methane wash treatment. H₂ is extracted from the syngas and produced impure and at low pressure from the membrane. The cold box then treats the required quantity of H₂. However, such methods are limited by equipment sizing and power consumption. Prior art solutions related to this method are economical only when the excess of H₂ is large enough so that the savings on cold box can justify the additional cost of the membrane and retrofitting of the facility. As well, prior art solutions of this type remove an H₂ stream that contains a CO concentration of about 1-2 %, thereby decreasing the CO production.

[0007] Another prior art solution is to treat all the syngas in a cold box. The entire H_2 flow is washed in the methane wash column so that most of the CO is extract-

ed from the H₂. The H₂ is extracted and a first portion of the H₂ product is produced under pressure and a second portion is expanded in a cryogenic expander to produce refrigeration. However, prior art methods of this type do not produce adequate refrigeration when the volume of the second portion is relatively small, consequently increasing power consumption is required when there are only small amounts of H₂ in the syngas.

[0008] Other prior art examples of improving CO recovery are illustrated in US-A-4888035 and EP-A-0895961. These documents describe processes for increasing CO recovery from a stripper column by an additional injection of CH₄ as a wash liquid in the stripper column. The US-A-4888035 teaches and discloses the use of a regenerated CH₄ stream that is removed from a flash column and injected into the stripper column above the feed from the wash column to increase CO recovery from the syngas. However, these patents do not teach or suggest the use of intermediate withdrawal of a portion of the H2 from a point intermediate on a methane wash column to reduce an amount of liquid methane required to wash a hydrogen product. Furthermore, US-A-4888035 does not teach or suggest procedures and or structures for the reduction of power consumption and capital expenditure reduction. EP-A-0895961 discloses the use of a feed of a H₂/CH₄ liquid from the wash column to wash the CO in the stripper column. This application is directed at CO loss and power conservation by removing an intermediate stream from the bottom stage of the methane wash column to provide impure methane reflux to the top of the hydrogen stripping column. EP-A-0895961 states that the process it describes is an improvement over US-A-4888035 because EP-A-0895961 discloses using an impure methane reflux from the wash column which is rich in CO, thereby allowing for savings in methane. The author of EP-A-895961 recognizes that the procedure requires a greater amount of methane for washing the CO, but states that the amount of methane used would be less than the amount required for US-A-4888035 which would result in power savings of between 2 to 4 % as compared to equivalent CO content in the reject hydrogen stream of the US-A-4888035. However, EP-A-0895961 still requires extra capital expenditure for a large pump and costs associated with the operation of the pump. Accordingly, the art field is in search of a method of enhancing CO recovery from syngas without excessively increasing energy consumption and/or costs. Another prior art solution for enhancing CO recovery from syngas is disclosed in EP-A-1074510. The patent_application_discloses_a_process_and_system whereby hydrogen and carbon monoxide are separated from a condensate-containing gaseous mixture by using a first stripping column to lower the hydrogen content of the CO loaded methane stream obtained by washing CO from the gaseous mixture ascending a methane wash column and a second stripping column to lower the hydrogen content of the feed gas condensate ob-

tained from the methane wash column or phase separation. The vapor stream from the second stripping column or flash separator is fed to the first stripping column. The liquid stream from the first and second stripping columns are fed to different locations on a gaseous carbon monoxide separation column whereby a gaseous CO product stream is removed and a methane wash recycle stream is removed. The process is stated as improving the efficiency of the separation of the CO by avoiding the dilution of the CO with the CO loaded methane stream. However, the patent still requires large pumps for pumping the methane, thereby increasing capital expenditures and energy consumption. Accordingly, the art field is in search of a method whereby capital expenditures may be reduced and energy consumption may be reduced while still obtaining high CO recovery. As well, the art field is in search of a method whereby CO flow rates may be increased while producing high purity CO.

[0009] The present invention generally relates to methods and apparatuses for the treatment of syngas for the production of carbon monoxide, H_2 and/or related gases. Generally, CO stream production from a syngas treatment facility may be enhanced by withdrawing at least one H_2 rich stream from an intermediate point or points on a wash column associated with the syngas treatment facility.

[0010] According to the invention, there is provided a process for improving the separation of a feed gas comprised of at least carbon monoxide and hydrogen wherein the mixture is washed with liquid methane to separate, at least partially, a first carbon monoxide rich stream and a first hydrogen rich stream in a wash column, the first carbon monoxide rich stream is further separated into a second carbon monoxide rich stream, and the second carbon monoxide rich stream is stripped into a third carbon monoxide rich stream wherein the improvement comprises the step of

withdrawing at least one second hydrogen rich stream from the wash column at a location intermediate of the first hydrogen stream and the first carbon monoxide stream. The first, second and third carbon monoxide rich streams are rich in carbon monoxide with respect to the syngas stream. The first hydrogen rich stream is rich in hydrogen with respect to the syngas stream.

[0011] According to further optional aspects of the invention, the process further comprises:

- withdrawing at least one methane rich stream from the wash column at a location intermediate of the hydrogen stream and the carbon monoxide stream
- feeding at least a portion of the methane rich stream to a flash column associated with the process.

[0012] Preferably the feed gas consists primarily of 55 carbon monoxide and hydrogen.

[0013] At least one hydrogen rich stream is expanded to provide refrigeration, that stream preferably being the

at least one second hydrogen rich stream.

[0014] According to one embodiment, the first carbon monoxide stream is split into a first and a second substream. Preferably, the first substream is subcooled and injected into another column and/or the second substream is vaporized and injected into another column.

[0015] Preferably the second hydrogen rich stream is about 15 % to 50 % by volume of the total hydrogen flow

contained in the syngas and/ or contains at least 90 mol. % hydrogen, preferably at least 95 mol. % hydrogen,

still more preferably at least 98 mol. % hydrogen. [0016] Preferably the first hydrogen rich stream is withdrawn at the top of the wash column.

[0017] Preferably the first hydrogen rich stream is withdrawn with a carbon monoxide content of less than 1 ppm.

[0018] Preferably the third carbon monoxide rich stream is about 92 % to about 99 % by volume of the carbon monoxide in the feed gas.

[0019] The carbon monoxide/ methane distillation column may operate at between 8 and 10 bar abs.

[0020] According to a further embodiment of the invention, there is provided an apparatus for the separation of carbon monoxide gas and hydrogen from a gaseous mixture comprising:

- a methane wash column;
- a hydrogen flash column;
- a carbon monoxide/methane distillation column;
- at least one conduit means for feeding a feed gas comprising at least carbon monoxide and hydrogen to the wash column;
 - at least one conduit means for feeding a first carbon monoxide rich stream from the wash column to the at least one location about the flash column;
 - at least one conduit means for feeding a second carbon monoxide rich stream from the flash column to the stripping column; and,
 - the at least one conduit means provided intermediate on the wash column for withdrawing a second hydrogen stream.

[0021] According to further optional aspects of the invention, the apparatus comprises:

- at least one second conduit means for withdrawing at least one methane enriched stream from the wash column and injecting the at least one methane enriched stream into the flash column.
- at least one conduit means for feeding a second carbon monoxide rich stream from the flash column to at least one location about the distillation column comprises a first and a second conduit means whereby the second stream is divided into a first substream and a second substream.
 - means for injecting the first substream at a location about the distillation column and means for injecting the second substream at a location on the distilla-

30

tion column below the first substream.

an expander connected to the conduit means for extracting the second hydrogen product.

[0022] Preferably the second hydrogen rich gas is withdrawn between 10 and 20 theoretical trays below the top of the column. However the second hydrogen rich gas may be withdrawn at any intermediate point of the column.

[0023] According to a further aspect of the invention, there is provided a process for separating a carbon monoxide stream from a feed gas comprising at least carbon monoxide and hydrogen comprising the steps of:

separating a third carbon monoxide rich stream from the feed gas in a system comprising a wash column, a flash column, and a stripping column wherein the feed gas is separated into a first carbon monoxide rich stream, a first hydrogen rich stream, and a second hydrogen rich stream in the wash column, the first carbon monoxide rich stream is further separated into a second carbon monoxide rich stream in the flash column, the second carbon monoxide rich stream is further separated into a third carbon monoxide rich stream in the stripper column whereby the volume of the carbon monoxide in the third carbon monoxide rich stream is about 92 % to about 99 % of the volume of the carbon monoxide in the feed gas and the extraction of the second hydrogen rich stream reduces an amount of methane required to wash the feed gas.

[0024] For a further understanding of the nature and objects of the present invention, reference should be made to the following detailed description, taken in conjunction with the accompanying drawings, in which like elements are given the same or analogous reference numbers and wherein:

Fig. 1 is an illustration of an embodiment of an apparatus of the present invention.

Fig. 2 is an illustration of an alternative embodiment of an apparatus of the present invention.

Fig. 3 is an illustration of an alternative embodiment of an apparatus of the present invention.

Fig. 4 is an illustration of an alternative embodiment of an apparatus of the present invention.

Fig. 5 is an illustration of an alternative embodiment of an apparatus of the present invention.

[0025] Referring now to Fig. 1, an illustration of an embodiment of an apparatus of the present invention, a common cold box process using a methane wash is disclosed. The process provides for production of a carbon monoxide rich gas and/or production of a hydrogen rich gas. An embodiment of a cold box process of the present invention utilizes a methane wash column 2, a flash column 5 and a distillation column 11, sometimes

referred to as a stripper or stripping column 11.

[0026] A feed gas stream 1 to embodiments of the present invention generally comprises a stream containing at least carbon monoxide and hydrogen, such as syngas. The feed gas is cooled, dried and carbon dioxide ("CO2") is withdrawn by any method common in the art and feed gas 1 is passed through heat exchanger 17 after carbon dioxide removal and drying. Feed gas stream 18 is then passed into the bottom of methane wash column 2 by a conduit operating at between 10 and 40 bar abs, typically between 15 and 35 bar abs. The methane wash column 2 contains 40 theoretical trays. The feed gas stream 1 rising in column 2 is brought into gas-liquid contact in a countercurrent state with reflux methane ("CH₄") rich liquid flowing down from above. As a result, the downward liquid flow is gradually enriched in components whose boiling points are higher than that of hydrogen to become a carbon monoxide rich liquid. In the same manner, upward rising vapor is gradually enriched in hydrogen to become a hydrogen rich gas. A first hydrogen rich stream 3 is extracted at the top of the column 2 by a conduit. First hydrogen stream 3 may be extracted as a product, warmed through heat exchanger 17 before extraction as a product, used further in the process(es), expanded and used to recover energy and/or for any other purpose common in the art.

[0027] At least one second gaseous hydrogen rich stream 20 is extracted from at least one upper intermediate portion of column 2 by a conduit at a point 10 theoretical trays below the top of the column 2. The at least one second gaseous hydrogen rich stream 20 contains at least 90 mol. % hydrogen, preferably at least 95 mol. % hydrogen, still more preferably at least 95 mol. % hydrogen. Extracting at least one second hydrogen rich stream reduces the amount of methane required in the wash column. As well, an intermediate extraction will increase carbon monoxide recovery by decreasing the amount of methane required for washing of feed gas stream 1 which consequently allows for a higher pressure in flash column 5. Further, reduction in the amount of methane required for washing allows for smaller sized of columns for a given volume of feed gas, thereby saving in capital expenditures and power consumption by the process. In various embodiments, experimental results have illustrated a total power consumption reduction by about 10 % to about 40 %. However, other power savings may be achieved. Second hydrogen stream 20 may be extracted as a product, warmed through heat exchanger 17 before extraction as a product, mixed with liquid methane to lower methane vaporization temperature, used further in the process, and/or for any other purpose common in the art. In Fig. 1, all the second hydrogen stream 20 is warmed in heat exchanger 17 and then expanded in expander turbine 16, before being warmed in the heat exchanger. In other embodiments, a portion of second hydrogen stream 20 may be expanded in expander 16 to provide refrigeration. Expanded

50

stream 20 may then be collected as an expanded hydrogen stream. In various embodiments, expansion of stream 20 can be used to replace and/or supplement a carbon monoxide/nitrogen expansion, thereby conserving a greater portion of the carbon monoxide for collection as a product. Other embodiments utilize other hydrogen stream withdrawals such that a multiple number of withdrawals may be performed. Moreover, the at least one withdrawal is not necessarily limited to an upper portion of column and may be performed elsewhere on column 2.

[0028] Various embodiments of the present invention may be used to remove varying percentages and/or contents of the total hydrogen in the syngas through the stream 20. In an embodiment, 15 % to 50 % of the total hydrogen in the syngas 1 is removed through stream 20. In an alternate embodiment, about 26 % of the total hydrogen in the syngas 1 is removed through stream 20. [0029] A second carbon monoxide rich stream 4, also usually containing methane, is withdrawn from the bottom of column 2 by a conduit. In various embodiments, stream 4 is at least partially liquid. Stream 4 may be flashed across a valve 9 before introduction to a flash column 5. In flash column 5, a portion of the remaining hydrogen in stream 4 is withdrawn as a third hydrogen rich stream 6 by a conduit. Stream 6 may be collected as a product or used for any other purpose, as herein

[0030] A portion of liquid in flash column 5 is withdrawn as stream 7 and introduced to a distillation column 11 operating at between 1.5 and 3 bar abs. by a conduit. In various embodiments, stream 7 is flashed across a valve 8 before being fed to column 11. Column 11 operates at between 8 and 10 bar abs. A third carbon monoxide stream 14 is extracted from an upper portion of column 11 by a conduit and methane, typically at least partially liquid methane, is withdrawn from a lower portion of column 11 by a conduit and recycled back to column 2, via conduit 15 after pumping in pump 10. In various embodiments of the present invention, the volume of carbon monoxide extracted in the third carbon monoxide stream is about 92 % to about 99 % by volume of the carbon monoxide in the feed gas.

[0031] The process uses a carbon monoxide refrigeration cycle in which carbon monoxide rich gas 14 from the top of the distillation column 11 is warmed in the heat exchanger 17, compressed in a cycle compressor and sent back to the heat exchanger. Part of the gas compressed in the compressor to an intermediate pressure is removed as the product gas and the rest is further compressed. Part of the gas is cooled to an intermediate temperature, expanded in a turbine and recycled to the compressor. The rest of the gas continues to be cooled in the heat exchanger 17, and is used to warm the bottom reboilers of the flash column 5 and the distillation column 11. The gas at least partially condensed by cooling in the bottom reboilers is sent to the top condenser of the distillation column 11 where it is evaporated and

rejoins the refrigeration cycle.

[0032] The embodiments of all the figures use the same refrigeration cycle which will not be described in each case.

[0033] Now referring to Fig. 2, an illustration of an alternative embodiment of a process and apparatus of the present invention, at least one intermediate hydrogen rich stream 31 is extracted from at least one intermediate portion of column 2 and collected as a product. The intermediate hydrogen rich stream 31 is gaseous and contains at least 90 mol. % hydrogen, preferably at least 95 mol.% hydrogen, still more preferably at least 95 mol. % hydrogen. The product collected may be warmed in a heat exchanger or collected from the column, as before mentioned.

[0034] Generally, a feed gas 18 is fed to wash column 2 wherein separation occurs through rectification as heretofore described wherein at least one first hydrogen rich stream 3 may be withdrawn and at least one second gaseous hydrogen stream 31 may be withdrawn. First stream 3 is usually withdrawn at an area about an upper portion of column 2 and second stream 31 is withdrawn about an area intermediate feed 18 and first stream 3. [0035] Now referring to Fig. 3, an illustration of an alternative embodiment of a process and apparatus of the present invention, an intermediate hydrogen rich stream 70 is extracted from at least one lower intermediate portion of column 62 and collected as a product and an intermediate hydrogen rich stream 71 is extracted from at least one other intermediate portion of column 62. The hydrogen rich stream 70 is gaseous and contains at least 90 mol. % hydrogen, preferably at least 95 mol.% hydrogen, still more preferably at least 95 mol. % hydrogen. However, various other embodiments utilize varying numbers of withdrawals intermediate of feed and first hydrogen product withdrawal.

[0036] Fig. 4 and 5 show elements and streams already described in the previous figures which will not be described in these figures, except where differences exist.

[0037] Now referring to Fig. 4, an illustration of an alternative embodiment of an apparatus of the present invention, enhanced carbon monoxide recovery and hydrogen stripping can be achieved by injecting a regenerated methane stream 75 which is removed from the bottom of distillation column 65, pumped in 67 and sent in part to an intermediate region of the flash column to further scrub out carbon monoxide that has remained in the hydrogen released during stripping in flash column 64. Regenerated methane may be injected at any location of flash column 64 above the feed from wash column 62. In various embodiments, a cooling trap 77 is below a feed point for the regenerated methane. However, such other and further embodiments may utilize differing arrangements and/or sources of methane for aid in further removal of hydrogen in flash column 64. This feature of injection of regenerated methane can be used in cases where there is no intermediate withdrawal

40

of hydrogen enriched fluid in the wash column 62.

[0038] Now referring to Fig. 5, an illustration of an alternative embodiment of an apparatus of the present invention, an alternative manner of increasing carbon monoxide production is illustrated. Stream 82, in various embodiments, a liquid, is withdrawn from column 62 from a lower portion and fed to flash column 64. In various embodiments, the mixture withdrawn may be reduced in pressure as needed and as is common in the art. A condensed crude stream 83, typically at least partially a liquid, is withdrawn from column 62 and fed to column 64. In various embodiments, stream 83 may be at least partially vaporized in a heat exchanger 63. In various embodiments, a reboiler 76 is used to provide a vapor to aid in stripping of hydrogen and carbon monoxide in column 64. Additionally, in various embodiments, a methane rich stream 81 for scrubbing may be withdrawn from column 62 and fed to an upper portion of column 64 to provide a wash liquid to the upper portion of column 64 to further aid in reduction of carbon monoxide losses in hydrogen withdrawn from column 64. Removal of a methane stream from column 62 allows for a greater reflux in the flash column and or distillation column to further aid in carbon monoxide recovery.

[0039] Other embodiments may withdraw a single stream from a wash column and then split the stream withdrawn before injection of the withdrawn stream into another column. For example, in an embodiment a stream is withdrawn from the wash column and split into a first and a second substream. The first substream is subcooled and injected into the flash column and the second substream is vaporized and injected into the flash column at a location below the injection of the first substream. Other embodiments withdraw a stream from the flash column and split the stream into a first and second substream. In this embodiment, the first substream is subcooled and injected into the distillation column and the second substream is vaporized and injected into the distillation column at a location below the injection of the first substream.

[0040] The present invention is also directed to methods and processes for enhancing production of hydrogen and carbon monoxide, as from syngas. Generally, the method comprises the steps of passing a feed gas, such as syngas, to a cold box system comprising a wash column, a flash column, and a distillation column; and, withdrawing at least one second hydrogen rich stream from an intermediate portion of the wash column. Additional embodiments of methods of the present invention may further comprise expanding a potion of the withdrawn second hydrogen rich stream for providing refrigeration for the process, another process or for other energy recovery. Other embodiments may include other uses for the withdrawn second hydrogen rich stream and/or other processes within the cold box system. Further, other embodiments utilize at least one methane rich vapor and/or liquid withdraw from a wash column to

provide reflux and/or aid in stripping hydrogen in a flash column.

[0041] In a further embodiment, the present invention is a process for improving the separation of a feed gas comprised of at least carbon monoxide and hydrogen wherein the mixture is washed with liquid methane to separate, at least partially, a first carbon monoxide rich stream and a first hydrogen rich stream, the first carbon monoxide rich stream is separated into at least a second carbon monoxide rich stream, the second carbon monoxide rich stream is further separated into a third carbon monoxide rich product stream wherein the improvement comprises the step of:

withdrawing at least one second hydrogen rich stream from the wash column at a location intermediate of the first hydrogen stream and the carbon monoxide stream.

20 Example

[0042] A classical methane wash cold box was established utilizing 27 bar absolute pressure resulting in an H₂ recovery of 5444 Nm³/h from feed syngas with a 5540 Nm³/h quantity of H₂. The CH4 wash required was 3400 Nm³/h to achieve less than 5 ppm CO in the purified H₂. Cycle power consumption was at 640 kW.

[0043] Utilizing these same conditions, an intermediate extraction of H₂-enriched gas at 1450 Nm³/h of H₂ allowed for an H₂ product of 4039 Nm³/h with less than 5 ppm CO to be extracted.

[0044] The intermediate extraction may serve as a product or be rejected into the atmosphere or burnt. The intermediate H₂ extraction reduces the amount of methane required to wash the syngas in the wash column. As a consequence the feed to the flash column and to the CO/CH₄ distillation column is reduced leading to both power consumption savings and investment savings. The methane wash recycle is reduced to 1900 Nm³/h, power consumption is reduced to 490 kW. The flash column pressure is increased from 8 to 9.7 bars abs thus increasing CO recovery from 95.39 % to 95.86 %

[0045] The quantity of CO lost in the intermediate withdrawal is inconsequential when compared to the improvement of CO recovery on the flash column. Decreasing the CH₄ wash recycle allows a lower portion of the flash column to be richer in CO. Therefore, it can be operated at a higher pressure for a given CO recycle pressure, thus allowing a lower CO loss at the top of the flash column and increasing CO recovery.

[0046] Decreasing the CH_4 wash flow also increases the H_2 recovery, i.e. an extraction of 1450 Nm^3/h from the intermediate portion still allowed recovery of 4039 Nm^3/h at an upper portion because less CH4 wash means less H_2 loss in the CH_4 .

[0047] Furthermore, an expansion of the withdrawn H₂ from the intermediate portion produced an additional

5

10

saving of 140 kW/h by replacing a traditional CO/N₂ expansion.

Claims

A process for improving the separation of a feed gas

 (1) comprising at least carbon monoxide and hydrogen wherein the feed gas is washed with liquid methane to separate, at least partially, a first carbon monoxide rich stream (4, 83) and a first hydrogen rich stream (3) in a wash column (2, 62), the first carbon monoxide rich stream is further separated into a second carbon monoxide rich stream (4), and the second carbon monoxide rich stream is stripped into a third carbon monoxide rich stream (14, 69) characterized in that it comprises the step of:

withdrawing at least one second hydrogen rich stream (20, 30, 70, 71) from the wash column at a location intermediate of the first hydrogen stream and the first carbon monoxide stream.

- The process of Claim 1 further comprising the step of withdrawing at least one methane rich stream (81, 82) from the wash column (62) at a location intermediate of the hydrogen stream and the carbon monoxide stream.
- The process of Claim 2 wherein at least a portion of the methane rich stream (81, 82) is fed to a flash column associated with the process.
- The process of any preceding claim wherein the feed gas (1) consists primarily of carbon monoxide and hydrogen.
- The process of any preceding claim wherein at least one hydrogen rich stream is expanded to provide refrigeration.
- The process of Claim 5 wherein the at least one second hydrogen rich stream (20) is expanded to recover energy.
- 7. The apparatus of any preceding claims wherein the second hydrogen rich stream is about 15 % to 50 % of the total hydrogen flow contained in the syngas and/or contains at least 90 mol. % hydrogen, preferably at least 95 mol. % hydrogen and/or is withdrawn in gaseous form.
- The apparatus of any preceding claims wherein a first hydrogen rich stream is withdrawn about an upper portion of the wash column (2, 62).
- The apparatus of Claim 8 wherein the first hydrogen rich stream is withdrawn with a carbon monoxide

content of less than 1 ppm

- 10. The apparatus of any preceding claim wherein a third carbon monoxide rich stream is about 92 % to about 99 % by volume of the carbon monoxide in the feed gas.
- 11. An apparatus for the separation of carbon monoxide gas and hydrogen from a gaseous mixture comprising:

a methane wash column (2, 62);

a hydrogen flash column (5);

a carbon monoxide/methane distillation column (11);

at least one conduit means (1) for feeding a feed gas comprising at least carbon monoxide and hydrogen to the wash column;

at least one conduit means (4) for feeding a first carbon monoxide rich stream from the wash column to the at least one location of the flash column;

at least one conduit means (7) for feeding a second carbon monoxide rich stream from the flash column to the stripping column; and, an at least one conduit means provided at an; intermediate point of the wash column (2) for withdrawing a second hydrogen stream (20, 30, 70, 71).

12. The apparatus of Claim 11 further comprising at least one second conduit means for withdrawing at least one methane enriched stream (81,82) from the wash column (62) and injecting the at least one methane enriched stream into the flash column (64).

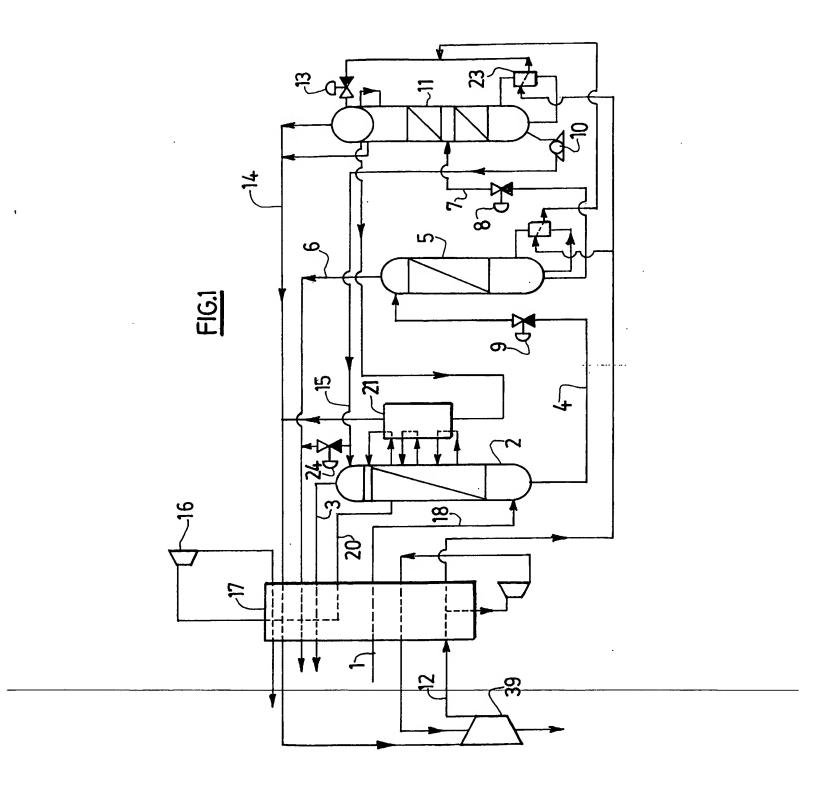
137 4

45

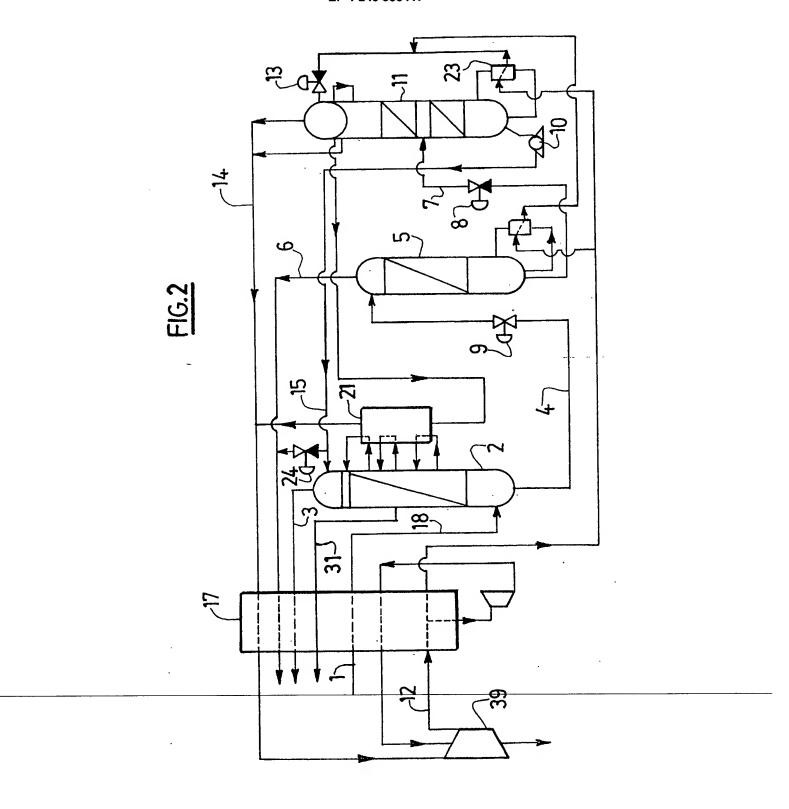
50

55

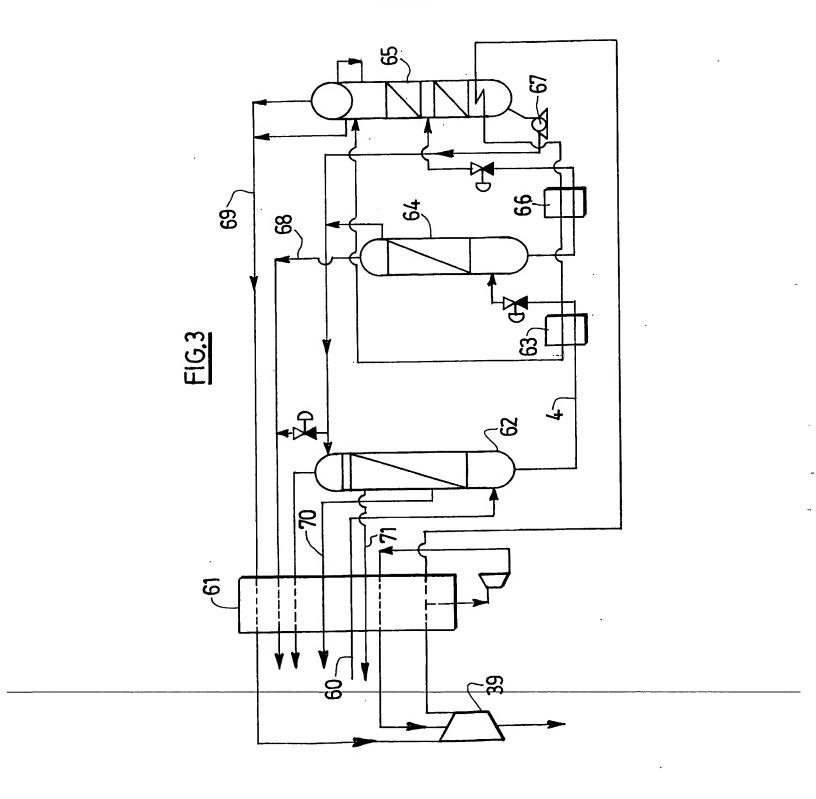
EP 1 245 533 A1



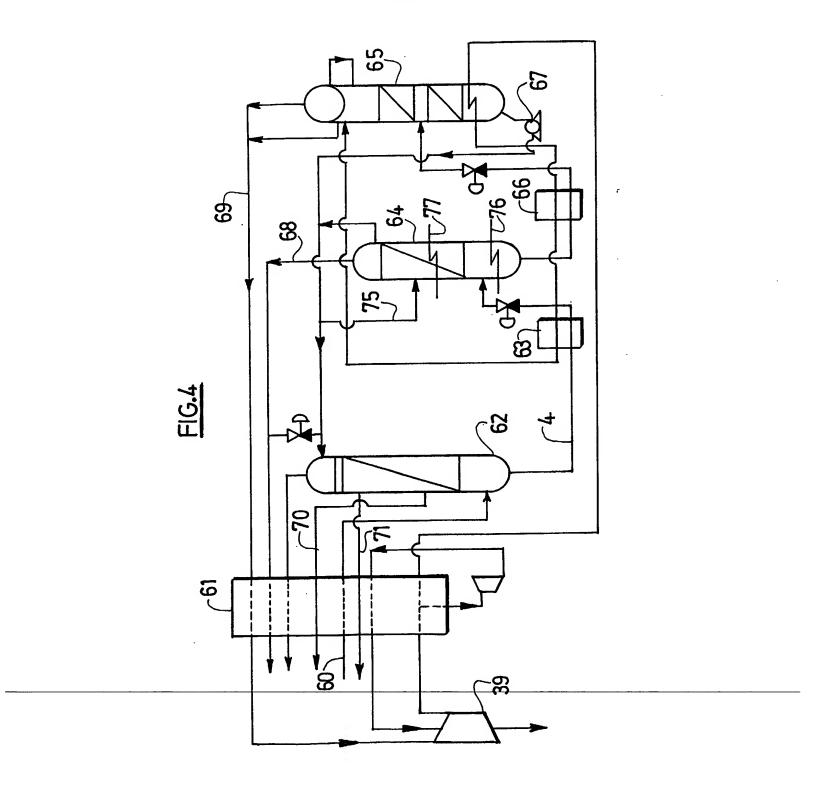
EP 1 245 533 A1



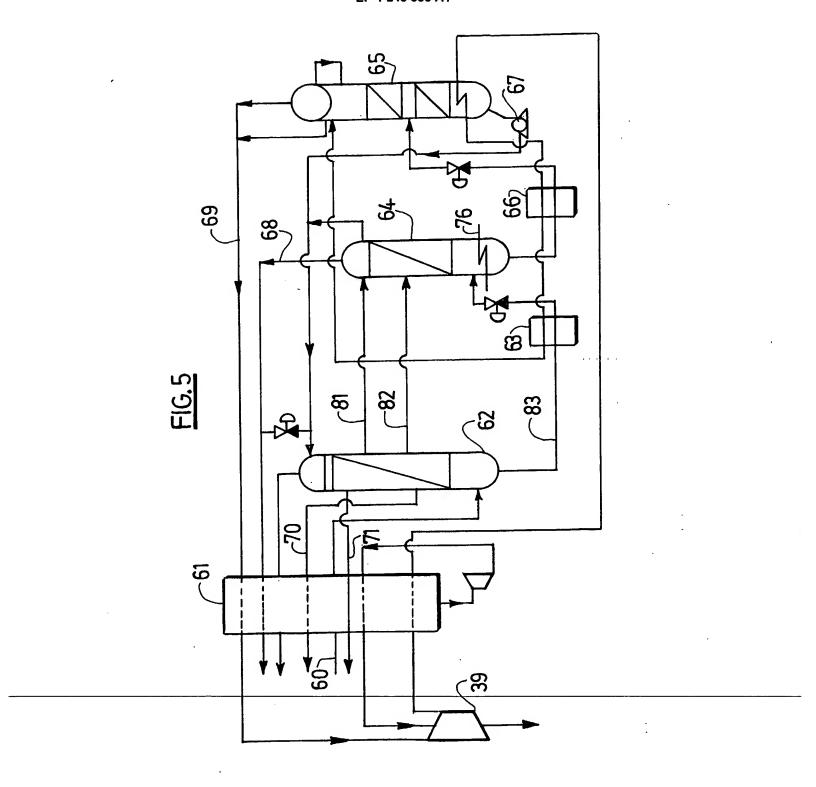
EP 1 245 533 A1



EP 1 245 533 A1



EP 1 245 533 A1



THIS PAGE BLANK (USPTO)

EP 1 245 533 A1



EUROPEAN SEARCH REPORT

Application Number EP 02 07 6094

	DOCUMENTS CONSID	PERED TO BE RELEVANT		
Category	Citation of document with of relevant pass	indication, where appropriate, sages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A,D	EP 0 895 961 A (AI 10 February 1999 (* page 2, line 29	R PROD & CHEM) 1999-02-10) - page 3, line 22 *	1,11	C01B3/50 F25J3/02
A,D	US 4 888 035 A (BAI 19 December 1989 (* column 1, line 4	UER HEINZ) 1989-12-19) 5 - column 2, line 60 *	1,11	
			:	TECHNICAL FIELDS SEARCHED (InLCI.7)
			,	C01B F25J
	The present search report has	been drawn up for all claims	119	
	Place of search	1	Examiner	
	BERLIN	10 June 2002	Cle	ment, J-P
X : partic Y : partic docui	TEGORY OF CITED DOCUMENTS cularly relevant if taken alone cularly relevant if combined with anot ment of the same category loological background	underlying the ir ument, but publis the application r other reasons	ivention shed on, or	

EP 1 245 533 A1

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 02 07 6094

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

10-06-2002

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
EP 0895961	A	10-02-1999	DE DE EP US	69800152 D1 69800152 T2 0895961 A1 6082134 A	21-06-2000 09-11-2000 10-02-1999 04-07-2000
US 4888035	Α	19-12-1989	DE DE EP	3739724 A1 3868021 D1 0317851 A2	08-06-1989 05-03-1992 31-05-1989

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82